

Origin of aromagnetism

M. A. Martsenyuk and N. M. Martsenyuk

A. M. Gor'kii Perm State University, 614600, Perm

(Submitted 24 December 1990; resubmitted 14 February 1991)

Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 5, 229–232 (10 March 1991)

An attempt is made to explain the aromagnetism observed by Tolstoï and Spartakov {*Pis'ma Zh. Eksp. Teor. Fiz.* **52**, 796 (1990) [*JETP Lett.* **52**, 161 (1990)]}. It is shown that this phenomenon is not of a magnetic nature. It occurs because the molecules of aromagnets have axial toroidal moments, which interact with the vortical electric field induced by the alternating magnetic field used in the experiments.

Tolstoï and Spartakov¹ have reported the observation of an interesting phenomenon which they called "aromagnetism." Microscopic crystals of several aromatic substances (anthracene, phenanthrene, etc.) suspended in water or some other liquid underwent a change in orientation in a magnetic field. This change was seen by observing a modulation of polarized light caused by the reorientation of the particles in an alternating magnetic field imposed on a suspension. The applied field was either a train of sign-varying pulses of fixed orientation or a rotating field of fixed amplitude. In the opinion of Tolstoï and Spartakov,¹ the effect can occur only if the particles have constant magnetic moments. At the same time, it is known that the molecules of the substances which were studied are not paramagnetic: They have neither a spin nor an orbital angular momentum. Another point which is not clear is just what sort of collective interaction might give rise to a magnetism of microscopic crystals.

In the present letter we show that the effect which was observed is of a nonmagnetic nature. All the experiments described in Ref. 1 were carried out in alternating fields, so the role of the external field with which the microscopic crystals actually interacted was played not by the magnetic field \vec{H} itself but by its time derivative $\dot{\vec{H}}$, which is equal to the curl of the electric field ($-\text{curl}\vec{E}$) according to Maxwell's equation. The vector $\dot{\vec{H}}$ differs from \vec{H} in that it is even under spatial inversion and time reversal, and it "works" only if the particles have moments of the same parity. Even-even moments of this sort were introduced by Dubovik *et al.*,² who called them "axial toroidal moments" \vec{G} . An example of a system which has a moment \vec{G} is a closed chain of electric dipole moments.

The energy of the interaction of a toroidal moment \vec{G} with a field $\dot{\vec{H}}$ is² $U = \lambda \vec{G}\dot{\vec{H}}/c = -\lambda \vec{G}\text{curl}\vec{E}$. Under the assumption that the vector \vec{G} is tied rigidly to the axis (\vec{e}) of the particle, i.e., $\vec{G} = G\vec{e}$, we can calculate the moment of force \vec{K} which acts on the particle in the field $\dot{\vec{H}}$: $\vec{K} = -[\vec{e}\nabla_e]U = -\lambda [\vec{G}\dot{\vec{H}}]/c$. In a viscous liquid, the equation of motion of the particle leads to the following expressions for the angular velocity of the particle, $\vec{\Omega}$, and the velocity at which the particle rotates around its axis, $\dot{\vec{e}} = [\vec{e}\vec{\Omega}]$ (we are ignoring inertia):

$$\vec{\Omega} = -\lambda[\vec{G}\dot{\vec{H}}]/c; \quad \dot{\vec{e}} = -\lambda G[\vec{e}\dot{\vec{H}}]/c. \quad (1)$$

These results agree qualitatively with the experimental data. In particular, they describe the effects (observed in Ref. 1) of the reorientation of the particles in the sign-varying field and the entrainment of the particles by the rotating field (cf. the solution of the corresponding equations for magnetized particles in Ref. 3). In a rotating field, there are two types of steady-state motion of the particles; a change in the type of motion occurs as the parameter ω/H is varied, where ω is the field rotation frequency. Assuming that the magnetic field is perpendicular to the rotation axis, we find from the expression $\dot{\vec{H}} = [\vec{\omega}\vec{H}]$ the results $\dot{H} = \omega H$ and $\omega/\dot{H} = 1/H$. In other words, in this case the magnetic field itself is playing the role of the parameter that determines the nature of the motion. In a weak field ($H < H_*$) the phase shift (α) between the axis of the particle and the field \vec{H} is fixed ($\alpha \approx \pi/2$), while in a strong field ($H \gg H_*$) the shift α becomes a function of H . This result does not contradict the observations in Ref. 1, which yielded $\alpha = \text{const}$ at $\omega/H = \text{const}$, but the data in Ref. 1 are not a sufficient basis for drawing any definitive conclusions.

We turn now to the proof that aromatic molecules have constant toroidal moments. The basic part of the molecule is a benzene ring with substituents X_A in place of hydrogen atoms (Fig. 1). Using the LCAO-MO method,⁴ we write the molecular orbital Ψ as a linear combination of s and p atomic orbitals of ring carbon atoms, $\phi_s(r_\alpha)$ and $\vec{r}_\alpha \phi_p(r_\alpha)$, and of σ orbitals of the substituents, $\zeta_A(r_A)$:

$$\Psi(\vec{r}) = \sum_{\alpha} [s_{\alpha} \phi_s(r_{\alpha}) + (\vec{p}_{\alpha} \vec{r}_{\alpha}) \phi_p(r_{\alpha})] + \sum_A q_A \zeta_A(r_A). \quad (2)$$

Here we are assuming that the vectors \vec{r}_{α} and \vec{r}_A start at the centers of the corresponding atoms; s_{α} , \vec{p}_{α} , and q_A are coefficients. The dipole moment \vec{d}_{α} of carbon atom α is calculated as the expectation value of the product $e\vec{r}_{\alpha}$ in state Ψ : $\vec{d}_{\alpha} = \langle \Psi | e\vec{r}_{\alpha} | \Psi \rangle$. The axial toroidal moment of the molecule, \vec{G} , was found as in Ref. 2 as half the sum of the vector products $[\vec{d}_{\alpha} \vec{R}_{\alpha}]$, where \vec{R}_{α} is the radius vector to the center of carbon atom α . Ignoring the overlap integrals of the atomic orbitals of neighboring atoms in a first approximation, we find from (2)

$$\vec{G} = eA \sum_{\alpha} s_{\alpha} [\vec{R}_{\alpha} \vec{p}_{\alpha}]; \quad A = \int r^2 \phi_s(r) \phi_p(r) dV. \quad (3)$$

We assume that the molecule is of symmetry D_{6h} and that the deviation from this symmetry can be dealt with by perturbation theory, as it customarily is in quantum chemistry.⁴ All the molecular orbitals are classified in terms of irreducible representations of the D_{6h} group. We are interested in only those orbitals that have a nonvanishing expectation value of the axial vector \vec{G} , which transforms under representations A_{1g} and E_{2g} (Ref. 5). This condition is satisfied by orbitals which transform under the two-dimensional representations E_{2g} and E_{1u} . Using group representation theory,⁵ we find (for example) that a molecular orbital of symmetry E_{2g} can be written in the form $\Psi_{E_{2g}} = 2(\psi_1 + \psi_4) - \psi_2 - \psi_3 - \psi_5 - \psi_6$, where $\psi_{\alpha} = s\phi_s(r_{\alpha}) + (p_1 x_{\alpha} + p_2 y_{\alpha})\phi_p(r_{\alpha}) + q\zeta_{\alpha}(r_A)$, and x_{α} and y_{α} are the projections of radius vector \vec{r}_{α} onto the axes of the local coordinate system (Fig. 1). From (3) we find $\vec{G} = 2eAR_0 s p_2 \vec{k}$, where \vec{k} is a unit vector running normal to the plane of the molecule, and R_0 is the radius of the molecule. Figure 1 shows the expectation values of the

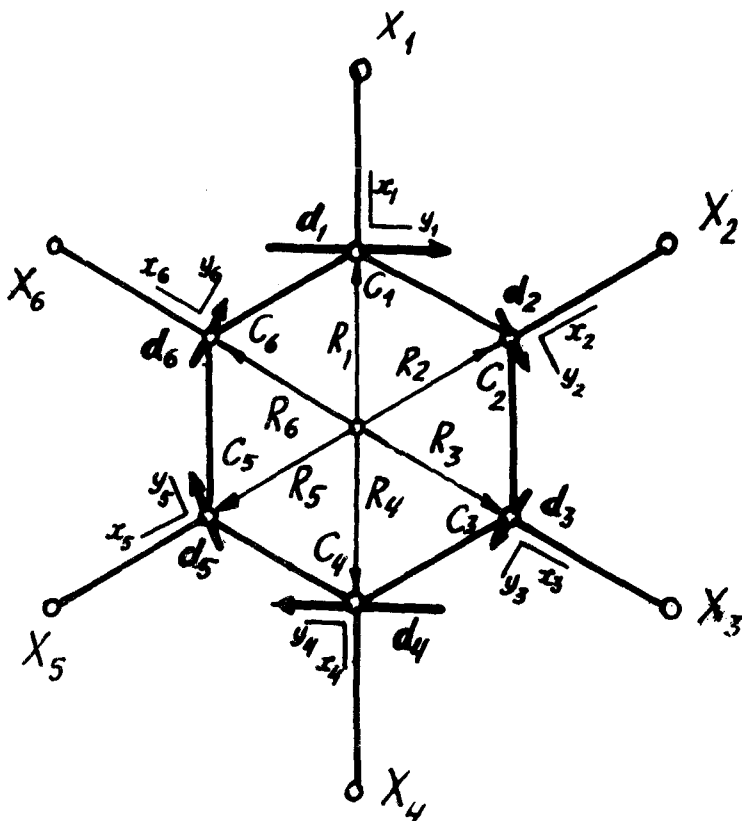


FIG. 1. Part of an aromagnetic molecule. The orientation of the axes of the local coordinate systems at the carbon atoms is shown by the light, mutually perpendicular lines. The heavy lines show the expectation values of the electric dipole moments of the carbon atoms of the benzene ring in the state $\Psi_{E_{2g}}$.

dipole moments of the carbon atoms in state $\Phi_{E_{2g}}$. In other words, in states with symmetry E_{2g} (and also with symmetry E_{1u} , as can be shown) the molecule has an axial toroidal moment \vec{G} , which is directed along the normal to the plane of the molecule.

We can now show that if planar aromagnetic molecules are stacked in a certain way, the interaction of the toroidal moments with each other will cause these moments to align parallel to each other, so an ordered arrangement ("ferromagnetic" or "weakly ferromagnetic") of these moments may arise in a microscopic crystal. We represent the molecule by a system of atomic dipole moments $\vec{d}_\alpha = \vec{d}(\vec{R}_\alpha)$ (here \vec{R}_α is the coordinate of atom α , reckoned from the center of the molecule; i.e., $\sum \alpha \vec{R} = 0$). In a first approximation, the function $\vec{d}(\vec{R}_\alpha)$ can be assumed a linear function of \vec{R}_α : $\vec{d}(\vec{R}_\alpha) = [\vec{g}\vec{R}_\alpha]$, where the vector \vec{g} is related in an unambiguous way to the toroidal moment. This relationship is $G_i = \sum [R_\alpha \vec{d}_\alpha]_i / 2 = I_{ik} g_k$, where we have introduced a form tensor of the molecule, $I_{ik} = \sum (R_\alpha^2 \delta_{ik} - R_{\alpha i} R_{\alpha k}) / 2$.

We now consider two identical planar molecules, lying in parallel planes. We

assume that their centers are connected by a radius vector \vec{R} (this configuration corresponds to the way in which planar molecules usually stack in a crystal). We assume that the moments of the molecules, \vec{G}_1 and \vec{G}_2 , are oriented perpendicular to their planes (we assume that these moments are directed along the normal \vec{k}), and we assume that one of the principal axes of the form tensor I_{jk} is also directed along \vec{k} . The two other principal axes of this tensor of one molecule are assumed to be parallel to the corresponding axes of the other. In this case the energy of the dipole-dipole interaction between molecules can be written in the form

$$V = -6G_{1z}G_{2z}[(I_1 - I_2)/I_3]^2\{R^4 - 5R^2(R_x^2 + R_y^2) + 35R_x^2R_y^2\}/R^9, \quad (4)$$

where R_x and R_y are the projections of the vector \vec{R} onto the principal axes of the form tensor, and I_i are the principal values of this tensor. In deriving (4) we took the limit $(R_z/R) \rightarrow 0$. It can be seen from the resulting expression that the interaction energy V is minimized when the projections G_{1z} and G_{2z} have the same sign, i.e., when the toroidal moments of the molecules, \vec{G}_1 and \vec{G}_2 , are parallel to each other, and the molecules are arranged in such a way that the expression in braces (curly brackets) in (4) is positive. In this case the interaction between electric dipoles promotes a "ferromagnetic" ordering of the axial toroidal moments in the lattice. We also note that aromatic substances have low-symmetry crystal lattices, of the triclinic or monoclinic system, which are consistent with a transition to a state with an axial toroidal order.² The transition temperature T_c can be estimated from the energy $V \sim G^2/R^5$, with $G \sim e\alpha R_0$, where $\alpha \approx 1 \text{ \AA}$ (the size of an atom), R_0 is the radius of the molecule, and R is the shortest distance between the planes of molecules in the lattice. For anthracene, for example, we would have $R_0 \approx 3 \text{ \AA}$ and $R \approx 6 \text{ \AA}$, so we find $T_c \sim V/k_B \sim 300 \text{ K}$.

¹N. A. Tolstoï and A. A. Spartakov, *Pis'ma Zh. Eksp. Teor. Fiz.* **52**, 796 (1990) [*JETP Lett.* **52**, 161 (1990)].

²V. M. Dubovik, L. A. Tosunyan, and V. V. Tugushev, *Zh. Eksp. Teor. Fiz.* **90**, 590 (1986) [*Sov. Phys. JETP* **63**, 344 (1986)].

³M. I. Shliomis, *Usp. Fiz. Nauk* **112**, 427 (1974) [*Sov. Phys. Usp.* **17**, 153 (1974)].

⁴M. J. Dewar, *Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969.

⁵L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)*, Nauka, Moscow, 1989. [Previous editions have been published in English translation by Pergamon, New York].

Translated by D. Parsons